論 文 の 内 容 の 要 旨

論文題目　Grain Boundaries and Dislocations of Titanium Dioxide

（二酸化チタンの結晶粒界と転位構造）

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Titania (TiO_2), a wide-band-gap semiconductor (~3 eV), finds applications in a wide variety of technological fields. In many of its applications, the two major types of defects, grain boundaries (GBs) and dislocations are known or suspected to affect functionalities of TiO_2. In addition to their distinct structures from their bulk counterparts, GBs and dislocations themselves may serve as effective sinks for point defects and chemical impurities, possibly giving rise to their structural modification and hence property shift of TiO_2. Despite their pivotal importance, their structures are still unknown especially at the atomic resolution in that resolving sites and chemical identification of all atoms comprising GBs and dislocations still pose a significant challenge. This issue should be especially pronounced for TiO_2, where the determination of oxygen is a nontrivial task particularly in the defective regions, hindering thereby the development of a general knowledge on how GBs and dislocations behave and influence properties of TiO_2.

In this work, I combine aberration-corrected high angle annular dark-field (HAADF), annular bright-field (ABF) scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), and first-principles calculations to obtain direct three-dimensional imaging of all the atoms in two commonly occurring Σ3 and Σ13 GBs (Σ stands for degree of geometrical coincidence at a GB) and

dislocations in a low angle tilt GB of TiO_2 with both atomic resolution and electronic sensitivity. The atomic-resolution structures of GBs and dislocations in TiO_2 are obtained and further related to electronic properties, upon which how properties of TiO_2 can be tailed by the linear defects is discussed.

I first characterize an individual Σ3 GB of TiO_2 before and after annealing at different atmospheres and demonstrate that the structural defects at GB stimulated by thermal treatment can be self-assembled to ordered superstructure, leading to GB nonstoichiometry and driving GB reconstruction at the atomic scale. Such a structural change is associated with electronic property shift of the GB, as the Ti atoms at GB show a valence state of +4 in the unannealed GB and the annealed one in vacuum, yet a mixed valence state of +3/+4 in the GB annealed at reduced atmosphere. I then investigate atomic structure and electronic properties of Σ13 GB and find that there appear very close Ti-O mixed columns on the mirror plane and that the Ti atomic columns on the mirror plane show a much weaker contrast in comparison to their bulk counterparts. Moreover, the EELS analysis reveals a possible phase transition from rutile TiO_2 in the bulk region to anatase TiO_2 at the Σ13 GB. Finally, the dislocations in two classes of bicrystals with different tilt angles have also been investigated. I have confirmed that periodic dislocations are indeed introduced into the boundary region in both bicrystals as I have designed. I obtain a direct atomic-resolution imaging of the dislocation core structure and show that the Ti atoms at the pristine dislocation core have a mixed valence state of +3/+4, giving rise to a conducting channel for each individual dislocation. In addition, atomistic calculations predict that there occur spin-polarized conducting states which are confined to within the dislocation core. The combined technique allows us to gain insights into complex atomic-scale structures and unusual physical properties of GBs and dislocations, which should be able to be applied to the detailed investigation of other species of linear and planar defects in a wide range of materials.